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American Society for Engineering Education
ONT Fellowship Programs
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Final Report to Office of Naval Technology Fellowship Program for
the period December 1 1987 - November 30 1988.

1. TOF/MPI/MS Investigation of Laser-assisted Organometallic
Deposition (ONT Proposal, 8 June 1987).

SUMMARY:

The multiphoton ionization/time-of-flight/mass spectrometry (MPI/TOF/MS) technique described in the ONT proposal has been demonstrated and applied to three photochemical systems: a) mechanistic studies of the laser-assisted chemical vapor deposition (LCVD) of gold from dimethyl gold hexafluoro acetyl acetonate (DMG hfac); b) LCVD of gallium from trimethyl gallium (TMG); and c) the detection of phenyl radicals from iodobenzene. A key aspect of the TOF/MPI/MS technique as a diagnostic is that it provides temporal selectivity in addition to wavelength and mass selectivity. This feature has been demonstrated quite dramatically in the gold, gallium and phenyl results. For example, we photolyzed iodobenzene adsorbed on a LiF substrate with 222 nm laser light to produce phenyl radicals and iodine atoms. The radical-radical recombination product, biphenyl, also was observed. Phenyl radicals were detected by laser ionization at 260 nm and iodine atoms in the $^2P_{3/2,1/2}$ ground state levels were detected at 279.617 and 280.895 nm, respectively. We were able to show that the phenyl radical signal determined by electron ionization has two contributions: one from the phenyl radicals produced directly by surface photolysis and a second from the fragmentation of the parent, iodobenzene, in the mass spectrometer ionizer. The temporal separation of these product distributions then makes it possible to estimate the degree of surface photolysis occurring as a function of such parameters as sample dosing and photolysis laser fluence.

PUBLICATIONS PENDING:

--Mechanism of the 222 nm Laser-assisted Decomposition of adsorbed DMG hfac, to be submitted to J. Vac. Sci. Tech. B.

--Photochemistry of $\text{Ga}(\text{CH}_3)_3$ at a Low-Temperature Surface, submitted to Advances in Laser Sciences - IV, 1989.

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--Low Temperature Laser-assisted Surface Decomposition of $\text{Ga}(\text{CH}_3)_3$, manuscript in preparation.

--A TOF/MPI/MS Study of the Photochemistry of Adsorbed TMG at 222 nm, to be submitted to Chem. Phys. Lett.

--TOF/MPI/MS Detection of the Phenyl Radical from by 222 nm Photolysis of Adsorbed Iodobenzene, to be submitted to J. Chem. Phys.

PRESENTATIONS:

--TOF/MPI/MS Study of the Decomposition of Adsorbed TMG on LiF and Quartz Surfaces at 222 nm, invited lecture, National Bureau of Standards, Gaithersburg MD, September 9 1988, Host: Howard Marary, Precision Engineering Division.

--Low Temperature Laser Assisted Surface Decomposition of $\text{Ga}(\text{CH}_3)_3$, contributed paper, Fourth International Laser Science Conference, Atlanta GA, October 3 1988.

--Resonance-enhanced Multiphoton Ionization Mass Spectrometric Studies of Surface Reactions Relevant to Microelectronic Fabrication Chemistry, invited lecture, Chemistry Department, Emory University, Atlanta GA, October 7 1988. Host: M. C. Lin.

--TOF/MPI/MS Studies of Surface Modification Chemistry, invited lecture, Semiconductor Processing Laboratory, Texas Instruments, Dallas TX, October 24 1988. Host: Duane Carter.

2. Determination of the molecular constants of the B $^1\text{B}_2$ state of SiF_2 from the 2+1 REMPI spectrum; internal energy determination of SiF_2 radicals produced by fluorine etching of silicon single crystals.

SUMMARY:

A two-photon MPI diagnostic for SiF_2 has been demonstrated and employed in studies of the silicon-fluorine etching system. Spectroscopic modeling of the REMPI bandshape has been performed in order to determine the internal energy content of the SiF_2 etch product. This measurement is the first of its kind for a polyatomic reaction product produced by a surface reaction.

- 2 -



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PUBLICATION PENDING:

--Rotational Temperature of SiF_2 Radicals Produced in the Thermal Etching of Silicon by Fluorine-containing Compounds, submitted to Advances in Laser Science - IV, 1989.

PRESENTATION:

--Rotational Temperature of SiF_2 Radicals Produced in the Thermal Etching of Silicon by Fluorine-containing Compounds, poster presented October 5, 1988 at the Fourth International Laser Science Conference, Atlanta GA.

3. The role of hydrogen in the decomposition of methane and acetylene and the formation of methyl radicals.

SUMMARY:

The formation of methyl radicals following the decomposition of CH_4 and C_2H_2 on a heated filament inserted into a quartz reaction tube has been monitored using multiphoton ionization mass spectrometry. The experiments were carried out under low pressure conditions, i.e. for the case in which the primary reaction products deposit on a (filament-heated) substrate nearby. The results indicate that methyl radicals are formed almost exclusively on the surface of the deposited carbon, and require substrate heating to desorb. Hydrogen was found to greatly enhance methyl radical production in these experiments; the effect has been shown to be noncatalytic. In addition, MPI was used to detect the species C, CH, CH_2 , C_2H_2 and C_2H_4 .

PUBLICATIONS PENDING:

--Mechanistic Studies of Methyl Radical Formation from the Heterogeneous Decomposition of Methane and Acetylene using Multiphoton Ionization Mass Spectrometry, manuscript in preparation.

--MPI/MS Detection of Methyl Radicals from the Decomposition of Acetylene, manuscript in preparation.

John A. Dagata.